Supporting Information

Mechanistic Study of the Oxidation of a Methyl Platinum(II) Complex with O_2 in Water: $Pt^{II}Me$–to–$Pt^{IV}Me$ and $Pt^{II}Me$–to–$Pt^{IV}Me_2$ Reactivity

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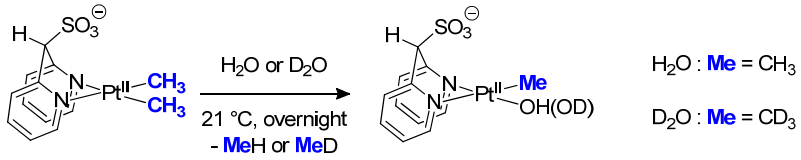
General Methods

All manipulations were carried out under argon atmosphere unless otherwise noted. All reagents for which synthesis is not given are commercially available from Aldrich, Acros, Alfa-Aesar or Pressure Chemicals, and were used as received without further purification. ^{1}H (400 MHz or 500 MHz) and ^{13}C NMR (100 MHz or 125 MHz) spectra were recorded on a Bruker AVANCE 400 or Bruker DRX-500. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. High Resolution Mass Spectrometry (HRMS) experiments were performed using a JEOL AccuTOF-CS instrument. The preparation and characterization of complexes **1**, **2**, **5**, **6**, **7, 8** and some of their deuterium isotopologues have been reported before.[1,2]

Preparation of K(dpms)Pt^{II}Me(OH/OD) (Me = CH_3, CD_3)



Scheme S1. Hydrolysis of K(dpms)PtMe_2 in water.

Stock solution of K(dpms)Pt^{II}Me(OH), Me = CH_3 [1] or CD_3 [2] was prepared under argon atmosphere via hydrolysis of K(dpms)Pt$^{II}(CH_3)_2$[1] (10.6 mg, 20.6 μmol) in 1.00 ml of degassed H_2O or D_2O, respectively. Reaction was carried out at ambient temperature overnight to give K(dpms)Pt^{II}Me(OH) in quantitative yield.

K(dpms)Pt$^{II}CD_3$(OD), 2-*d*$_3$. ^{1}H NMR (400 MHz, D_2O) δ: 8.84 (d, *J* = 6.5 Hz, 1H), 8.79 (d, *J* = 5.9 Hz, 2H), 8.04 (dt, *J* = 18.9, 8.9 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.55 (t, *J* = 6.9 Hz, 1H), 7.27 (dd, *J* = 11.0, 4.5 Hz, 1H), C*H*-SO_3 peak is not observed due to H/D exchange, 0.85 (br., residual signal Pt-CH_2D), 0.79 (br., residual signal Pt-CHD_2).

Independent Synthesis of *C*$_1$-*sym*-(dpms)Pt^{IV}(CH$_3$)(OH)(*axial*-CD$_3$)

Under argon atmosphere a solution of K(dpms)Pt^{II}CH$_3$(OH) (4.8 μmol) in D_2O was combined with CD_3I (0.30 μL, 4.8 μmol). The mixture was stirred for 5 minutes.

^{1}H NMR (400 MHz, D_2O) δ: 8.69 (d, J = 5.6 Hz, 1H), 8.54 (d, J_{Pt-H} = 41.7 Hz, 1H), 8.22 (t, J = 8.0 Hz, 2H), 8.00 (dd, J = 15.3, 8.1 Hz, 2H), 7.86 – 7.76 (m, 1H), 7.67 (t, J = 7.3 Hz, 1H), 6.40 (s, 1H, C*H*-SO_3), 1.66 (s, J_{Pt-H} = 66.5 Hz, 3H, Pt-C*H*$_3$).

Independent Synthesis of *C*$_1$-*sym*-(dpms)Pt^{IV}(CD$_3$)(OH)(*axial*-CH$_3$)

Under argon atmosphere a solution of K(dpms)Pt^{II}CD$_3$(OH) (3.1 μmol) in D_2O was combined with CH_3I (0.20 μL, 3.2 μmol). The mixture was stirred for 5 minutes.

^{1}H NMR (400 MHz, D_2O) δ: 8.69 (d, J = 6.0 Hz, 1H), 8.54 (d, J = 6.6 Hz, J_{Pt-H} = 41.5 Hz, 1H), 8.22 (t, J = 8.2 Hz, 2H), 8.00 (dd, J = 15.1, 8.5 Hz, 2H), 7.81(m, J = 7.3 Hz 1H), 7.67 (t, J = 7.7 Hz, 1H), C*H*-SO_3 peak is not observed due to H/D exchange, 1.97 (s, J_{Pt-H} = 78.9 Hz, 3H, Pt-C*H*$_3$).

Preparation of Buffer Solutions *pH* = 4.1 – 14.0

Table S1. Buffer composition, ionic strength and concentration.

Ionic strength	$C_{(buffer)}$	***pH***	Buffer Composition
0.27	0.14 M	**4.1**	10 mL of Solution A + 25.3 mL of Solution B + 14.7 mL of H_2O
0.36	0.07 M	**5.9**	88 mL of 0.0667M KH_2PO_4 + 12 mL Na_2HPO_4 of 0.0667M
0.34	0.07 M	**8.0**	5.5 mL of 0.0667M KH_2PO_4 + 94.5 mL of 0.0667M Na_2HPO_4
0.23	0.11 M	**10.0**	10 mL of Solution A + 9.0 mL of Solution B + 31 mL of H_2O
0.22	0.09 M	**11.9**	10 mL of Solution A + 0.2 mL of Solution B + 39.8 mL of H_2O
1.0	1.0 M	**14.0**	1 M KOH

Solution A: Citric acid 0.64 g (3.33 mmol), H_3PO_4 (85 %) 0.23 mL (3.33 mmol), H_3BO_3 0.35 g (5.7 mmol), NaOH (1M) 34.3 mL, 65.7 mL H_2O.

Solution B: 0.1 M solution of $HClO_4$.

Inertness of (dpms)$Pt^{II}Me(OH_n)^{(2-n)-}$ with respect to ligand exchange in buffer solutions.

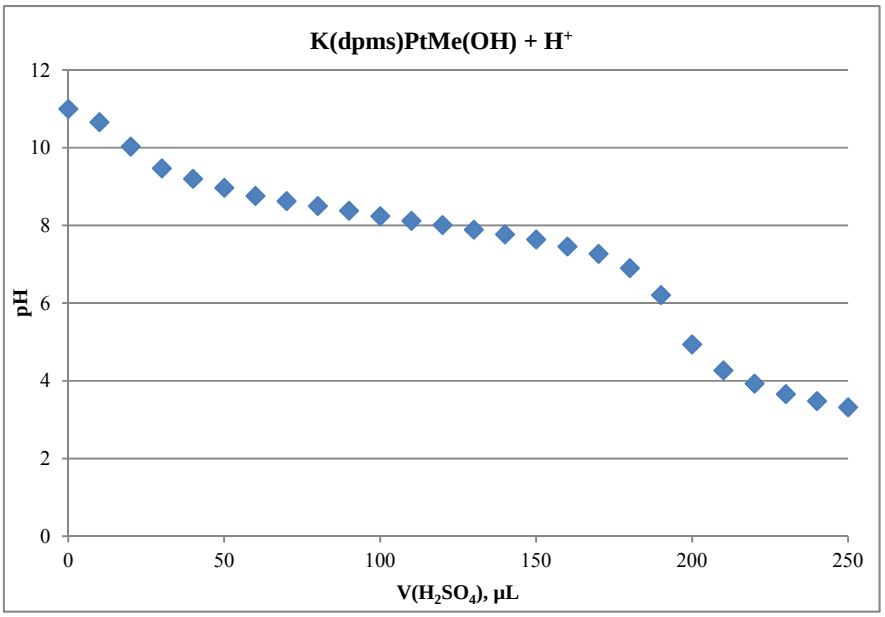
Control experiment. Under argon atmosphere of the glove box, solution of (dpms)$Pt^{II}Me(OH_2)$[1] (0.35 mL, 60 mM) in D_2O was combined with KH_2PO_4, (2.86 mg, 21.0 μmol) or Na_2HPO_4, (2.98 mg, 21.0 μmol). Reaction mixture was monitored by ^1H NMR spectroscopy. No changes to the (dpms)$Pt^{II}Me(OH_2)$ were observed over 24 hours.

Similar control experiment was performed with *pH* = 4.1, 10.0, 11.9 buffer. A solution of (dpms)$Pt^{II}Me(OH_2)$ (0.1 mL, 60 mM) in D_2O was combined with 0.5 mL of *pH* = 4.1, 10.0, 11.9 buffer. Reaction mixture was monitored for several days by ^1H NMR spectroscopy. No changes to the (dpms)$Pt^{II}Me(OH_2)$ were observed over three days.

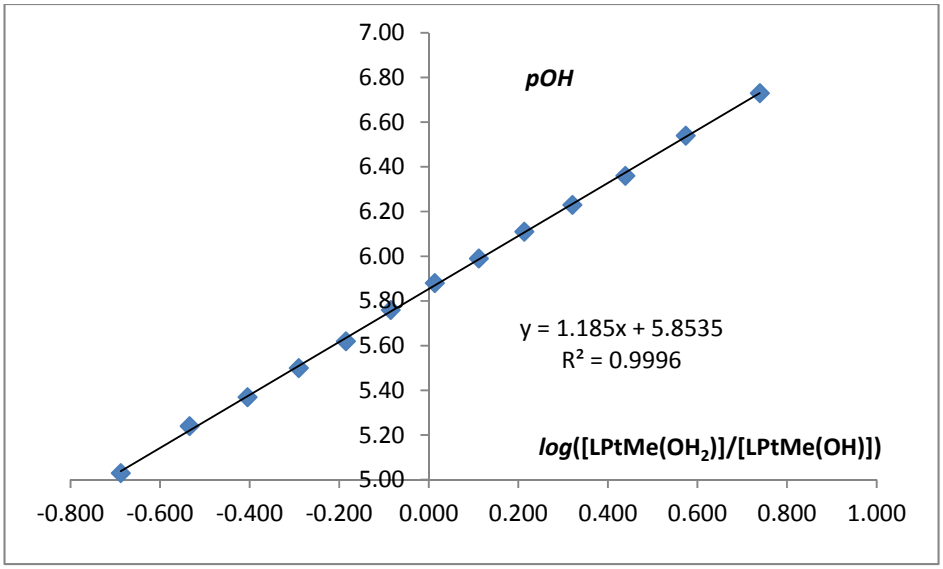
Determination of pK_a of (dpms)$Pt^{II}Me(OH_2)$

Under argon atmosphere aqueous K(dpms)Pt^{II}Me(OH) (1.0 mL, 0.01N) was placed in a vial with a stir bar and a rubber septum. The vial was taken out of the glove box and a digital *pH* meter probe was immersed into the solution. Titration was performed using 0.05 N H_2SO_4 in 10 µL aliquots.

pH	V(H_2SO_4) (µL)
11.00	0
10.66	10
10.03	20
9.47	30
9.20	40
8.97	50
8.76	60
8.63	70
8.50	80
8.38	90
8.24	100
8.12	110
8.01	120
7.89	130
7.77	140
7.64	150
7.46	160
7.27	170
6.90	180
6.21	190
4.94	200
4.27	210
3.93	220
3.66	230
3.48	240
3.32	250



This data was used to calculate the [$LPt^{II}Me(OH_2)$]/[LPt^{II}Me(OH)] ratio for each *pOH* value. Then using the linear regression of *pOH* – pK_b = *log*([$LPt^{II}Me(OH_2)$]/[LPt^{II}Me(OH)]) the pK_b value was found.

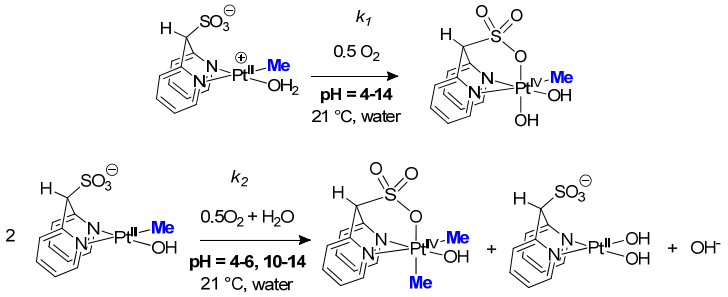


Slope = 1.19±0.01

Intercept 5.85±0.01 = pK_b;

pK_a = 8.15±0.01

Kinetics and product distribution in aerobic oxidation of K(dpms)Pt^{II}Me(OH) at *pH* = 4 - 14



Scheme S2.

General procedure. The oxidation of aqueous (dpms)Pt^{II}Me(OH$_n$)$^{(2-n)-}$ was run under vigorous stirring in a 25 mL round-bottom flask filled with O_2(*g*) equipped with a stirring bar and an O_2-filled balloon. The solution *pH* was maintained using buffer solutions (*pH* = 4.1, 5.9, 8.0, 10.0, 11.9) or 1.0 M KOH (*pH* 14.0). First, approximately 2.0 mL of ~3-17 mM stock solution of aqueous K(dpms)Pt^{II}Me(OH) were combined with an appropriate aqueous buffer or 1.00 M KOH under argon atmosphere. 3-17 equivalents of 2,2,6,6-tetramethylpiperidyl-N-oxyl (TEMPO) were introduced if necessary. The mixture was temperature-equilibrated and then injected with a syringe into the reaction flask placed in a temperature-controlled water-ethylene glycol bath at 21.0 °C. Vigorous stirring began immediately. Periodically a ~0.2 mL aliquot of the reaction mixture was taken with a syringe, transferred into argon-filled NMR tube, and diluted with 0.3 mL degassed D_2O to stop the reaction. Concentrations of the reactant, *C*$_1$-*sym*-(dpms)Pt^{IV}Me(OH)$_2$ and *C*$_1$-*sym*-(dpms)Pt^{IV}Me$_2$(OH) were monitored by ^{1}H NMR spectroscopy with 1,4-dioxane used as an internal standard. Methyl group balance was calculated based on the sum of representative aromatic or aliphatic protons. Minimum of two kinetics runs were performed.

Table S2. The half-life of the overall oxidation reaction of (dpms)$Pt^{II}Me(OH_n)^{(2-n)-}$, n=1, 2 (eq 1 plus 2) and product distribution at 21 °C in water.

pH	$t_{1/2}$, hrs	$t_{1/2}$, min	$LPt^{IV}Me(OH)_2$ (%)	$LPt^{IV}Me_2(OH)$ (%)
4.0	0.80 ± 0.03	48 ± 2	96 ± 1	2 ± 1
6.0	0.58 ± 0.03	34.5 ± 1.5	97 ± 1	1 ± 1
8.0	0.070 ± 0.003	3.9 ± 0.2	99 ± 1	0
10.0	0.22 ± 0.01	13 ± 0.6	98 ± 1	2 ± 1
12.0	3.3 ± 0.1	3 h 18 m ± 6 m	45 ± 2	51 ± 1
14.0	5.6 ± 0.3	5 h 36 m ± 18 m	30 ± 1	70 ± 1

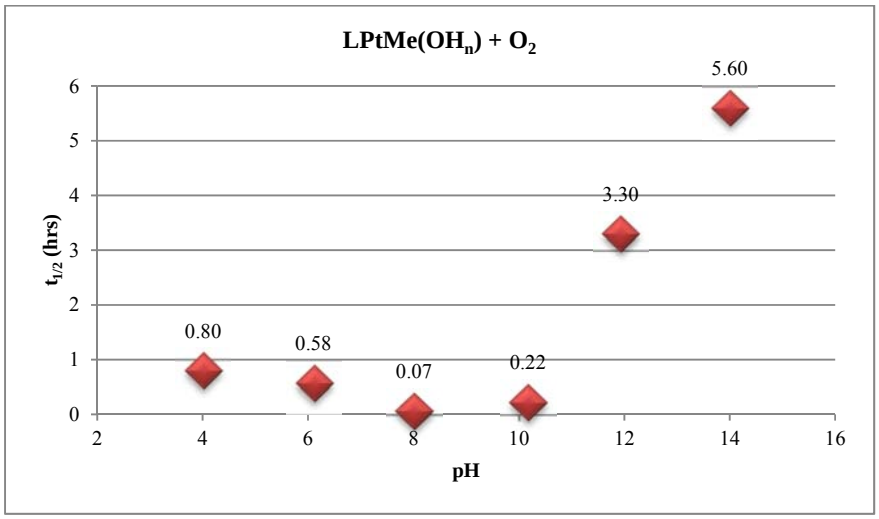


Figure S1. Half-lives of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=4.1-14.0**, at 21.0 °C

Kinetic plots of disappearance of the (dpms)$Pt^{II}Me(OH_n)^{(2-n)-}$, *n*=1, 2 at *pH* = 4.1 – 14, 21 °C

A. Reactions at *pH* 4.1

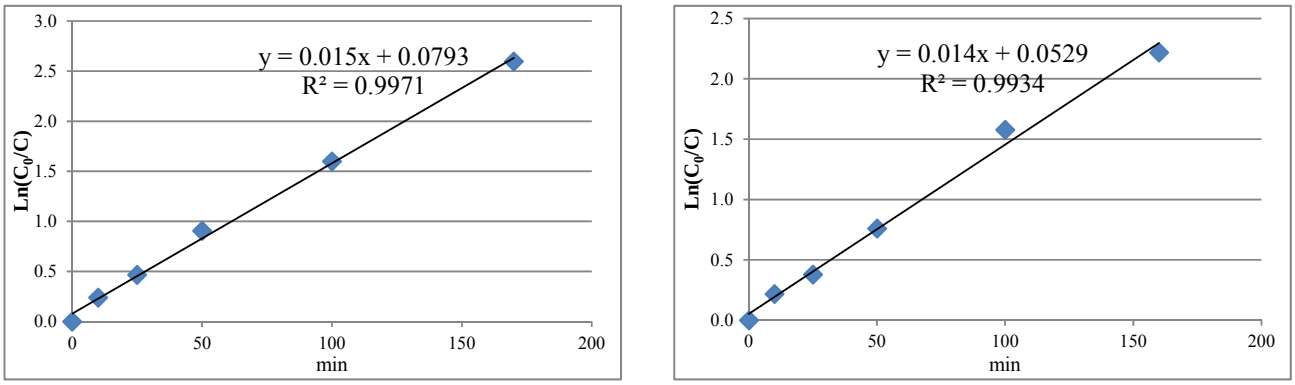


Figure S2. First-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=4.1**, at 21.0 °C.

[SM] = 4.4 mM, conversion = 93%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 91%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 2%
$t_{1/2}$ = 46 min

[SM] = 4.1 mM, conversion = 89%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 87%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 1.6%
$t_{1/2}$ = 50 min

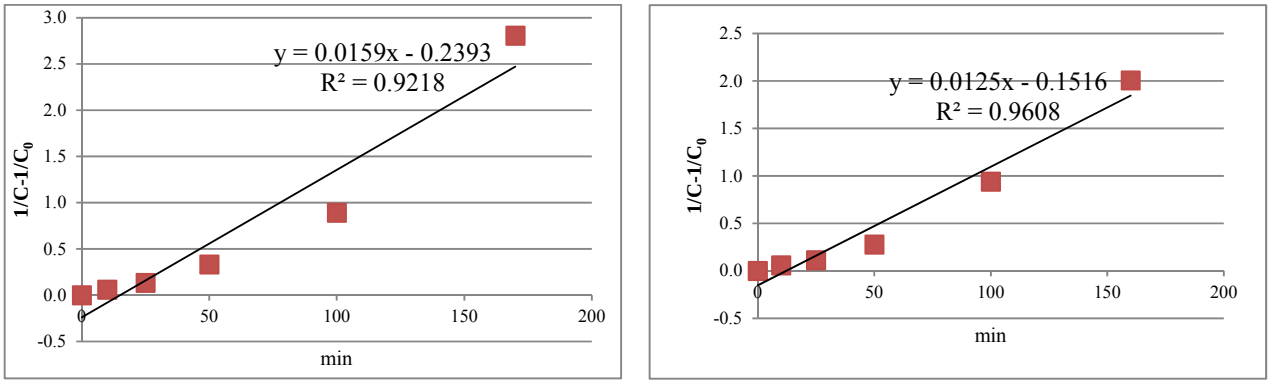
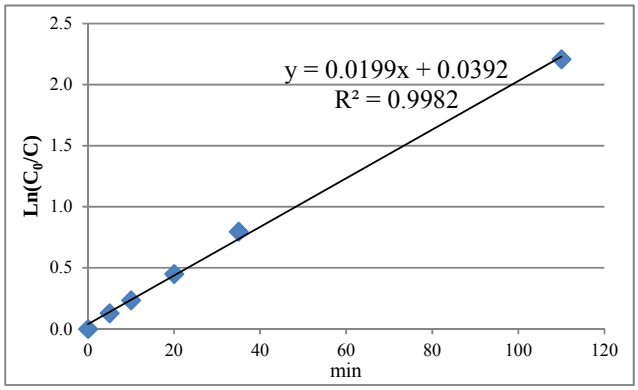


Figure S3. Attempted second-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH)$ at ***pH*=4.1**, at 21.0 °C.

B. Reactions at *pH* 5.9



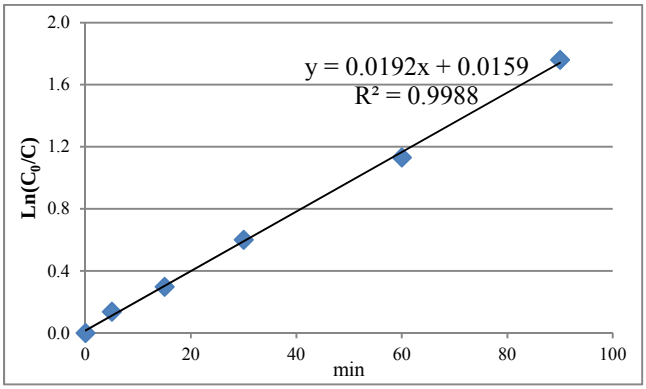
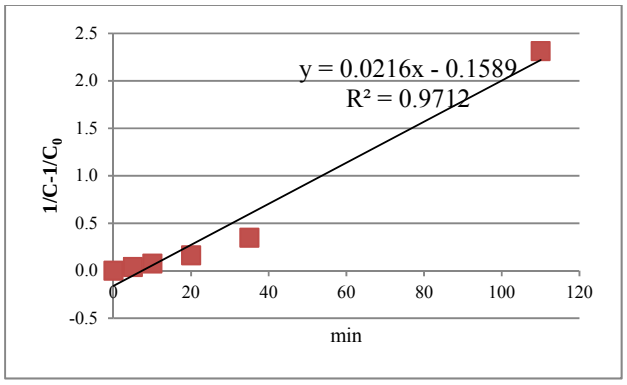


Figure S4. First-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=5.9**, at 21.0 °C.

[SM] = 3.5 mM, conversion = 89%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 88%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 1.4%
$t_{1/2}$ = 33 min

[SM] = 3.6 mM, conversion = 83%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 82%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 1.0%
$t_{1/2}$ = 36 min



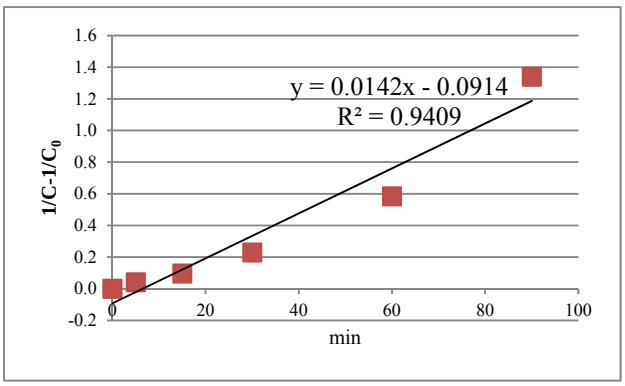
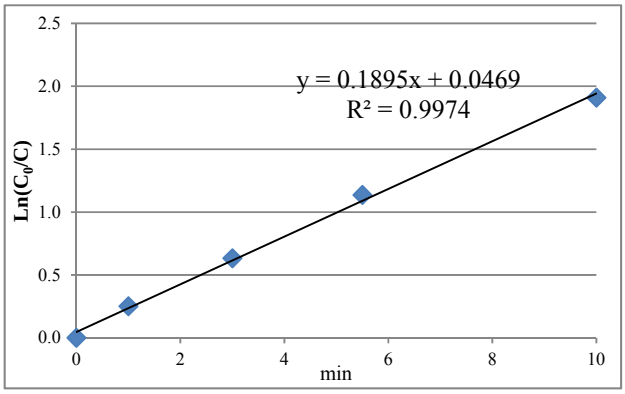


Figure S5. Attempted second-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH)$ at ***pH*=5.9**, at 21.0 °C.

C. Reactions at *pH* 8.0



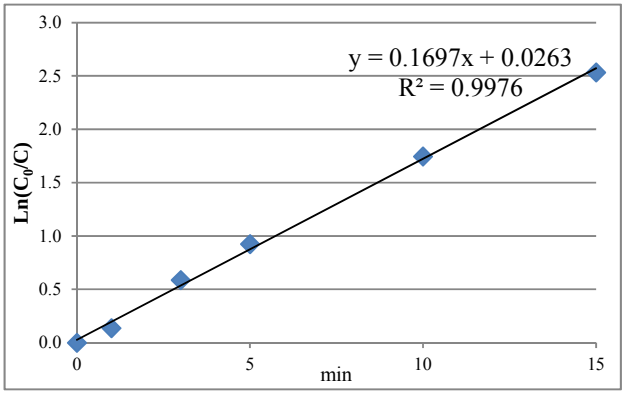
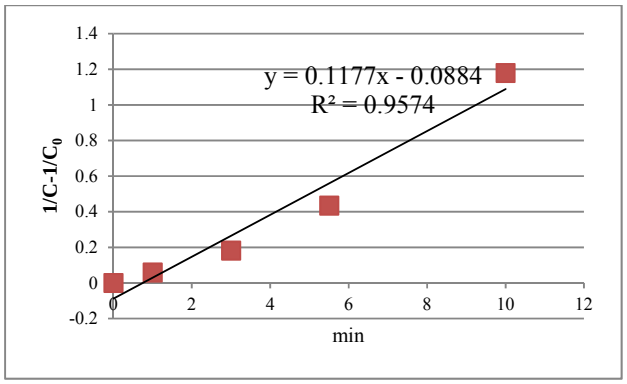


Figure S6. First-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=8.0**, at 21.0 °C.

[SM] = 4.9 mM, conversion = 85%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 85%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 0%
$t_{1/2}$ = 3.7 min

[SM] = 8.9 mM, conversion = 92%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 92%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 0.4%
$t_{1/2}$ = 4.1 min



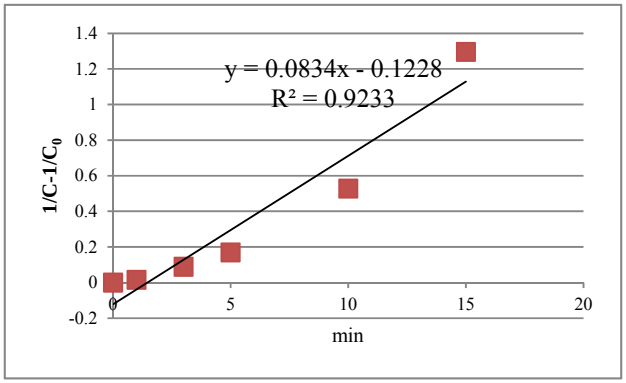


Figure S7. Attempted second-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=8.0**, at 21.0 °C

D. Reactions at *pH* 10.0

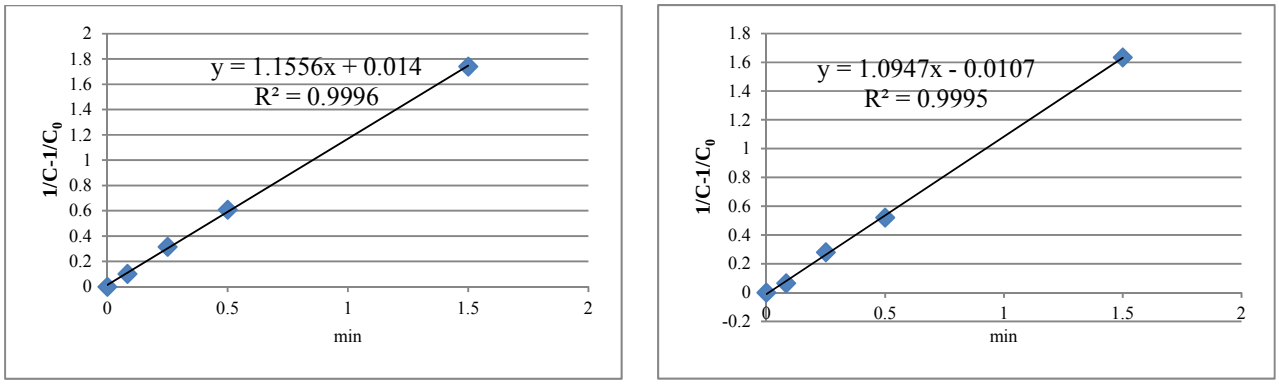


Figure S8. Second-order kinetics plots for disappearance of (dpms)Pt^{II}Me(OH) at ***pH*=10.0**, at 21.0 °C.

[SM] = 4.2 mM, conversion = 87%
(dpms)Pt^{IV}Me(OH)$_2$ yield = 85%
(dpms)Pt^{IV}Me$_2$(OH) yield = 2.5%
$t_{1/2}$ = 0.21 hrs

[SM] = 4.0 mM, conversion = 88%
(dpms)Pt^{IV}Me(OH)$_2$ yield = 86%
(dpms)Pt^{IV}Me$_2$(OH) yield = 2%
$t_{1/2}$ = 0.23 hrs

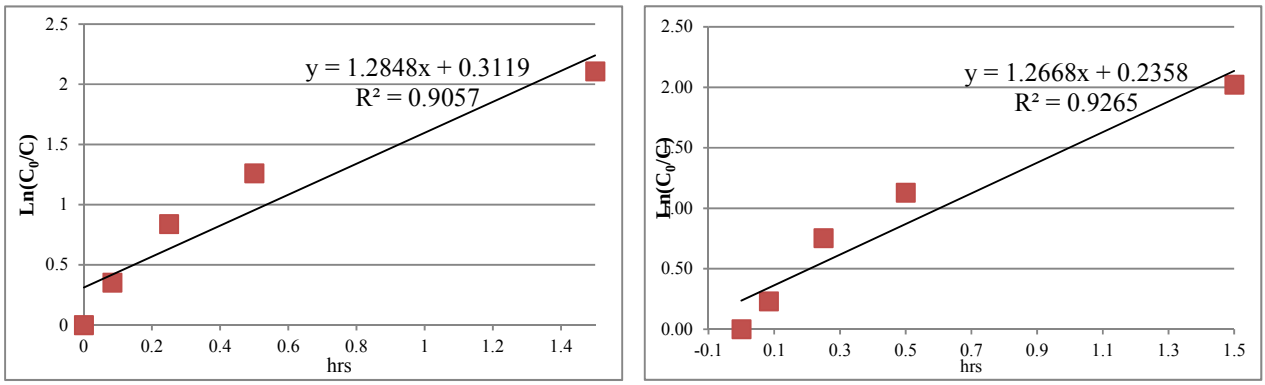
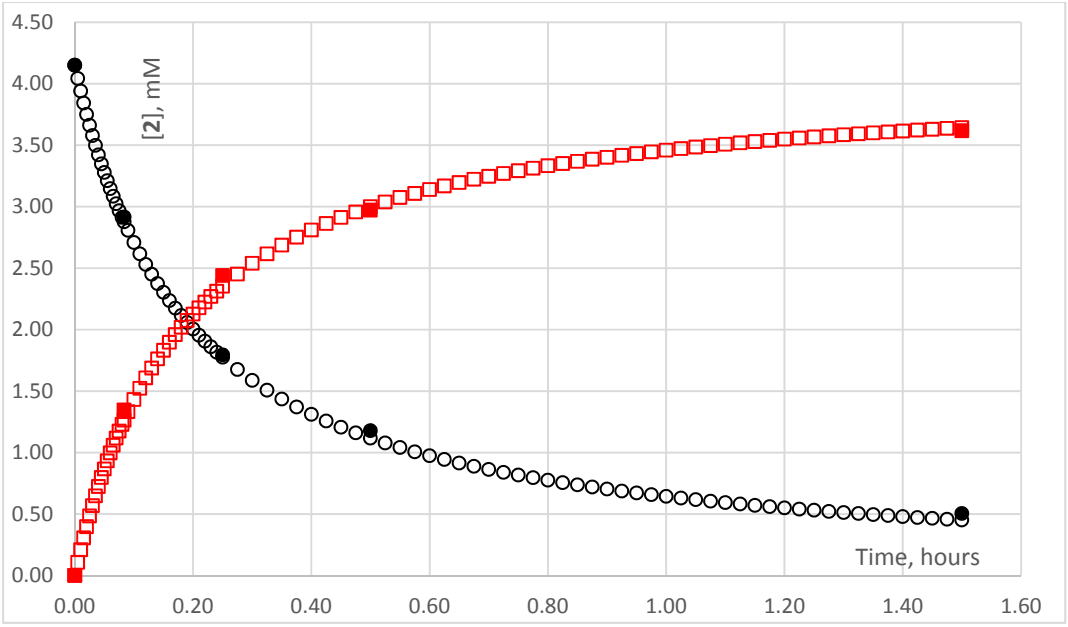


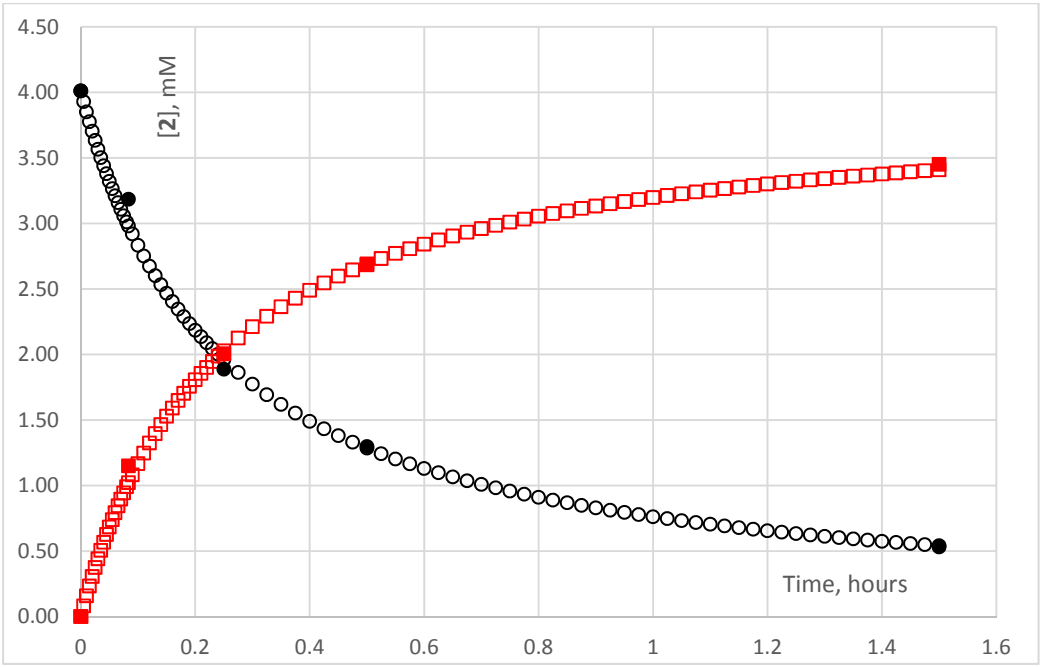
Figure S9. Attempted first-order kinetics plots for disappearance of (dpms)Pt^{II}Me(OH) at ***pH*=10.0**, at 21.0 °C.

Best least square fitting of the experimental data for *pH* = 10.0 achieved by numerical integration of the rate law $-d[2]/dt = k_{2,2nd\ order}[2]^2 + k_3[2]$

Circles – [**2**], squares – [**5**]. Empty figures represent calculated concentrations and filled ones – measured in experiment.

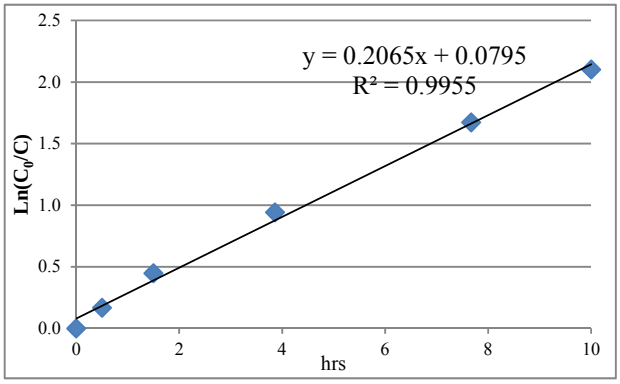


$k_{2,2nd\ order}$=	3.45E-01	$M^{-1}s^{-1}$		k_3=	9.17E-06	s^{-1}



$k_{2,2nd\ order}$=	2.80E-01	$M^{-1}s^{-1}$		k_3=	8.85E-06	s^{-1}

E. Reactions at *pH* 11.9



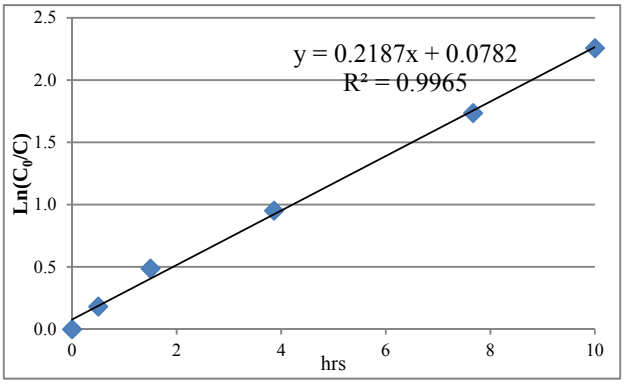
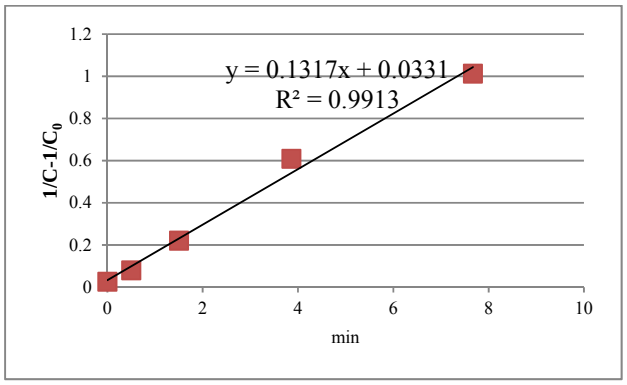


Figure S10. First-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=11.9**, at 21.0 °C.

[SM] = 7.1 mM, conversion = 87%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 43%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 44%
$t_{1/2}$ = 3.4 hrs

[SM] = 8.0 mM, conversion = 90%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 46%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 43%
$t_{1/2}$ = 3.2 hrs



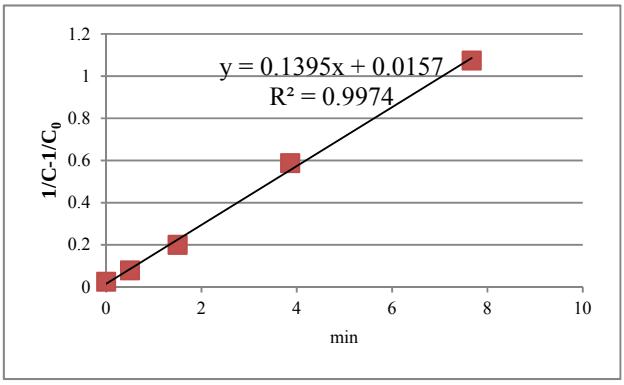
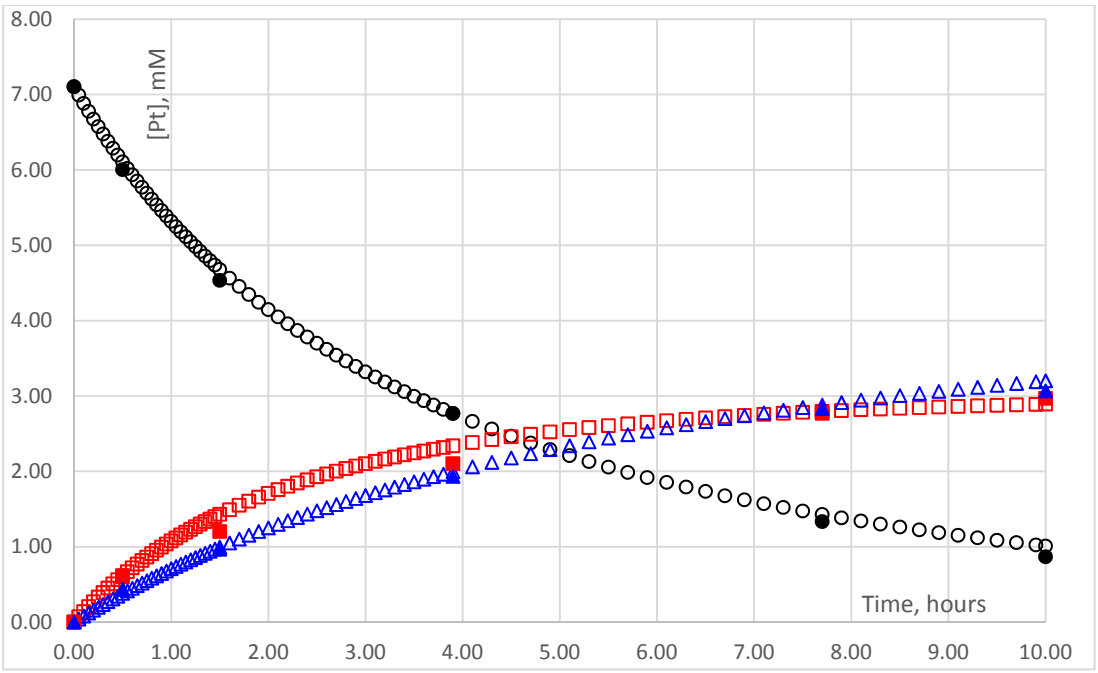


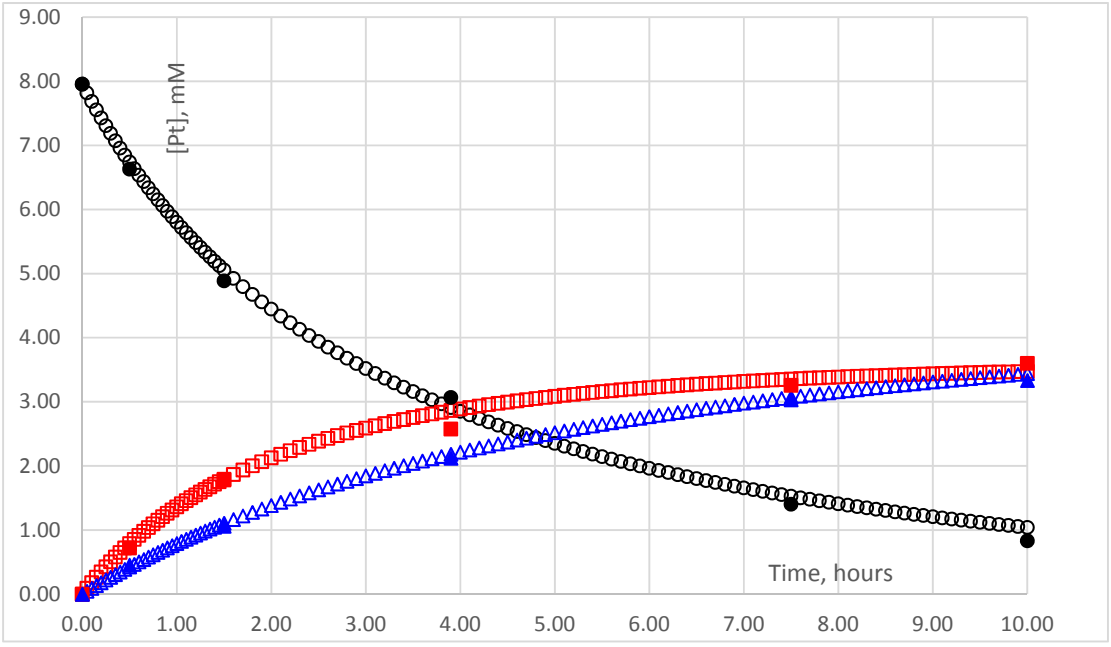
Figure S11. Second-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH)$ at ***pH*=11.9**, at 21.0 °C.

Best least square fitting of the experimental data for *pH* = 11.9 achieved by numerical integration of the rate law $-d[2]/dt = k_{2,2nd\ order}[2]^2 + k_3[2]$

circles – [**2**], squares – [**5**], triangles – [**6**]. Empty figures represent calculated concentrations and filled ones – measured in experiment.

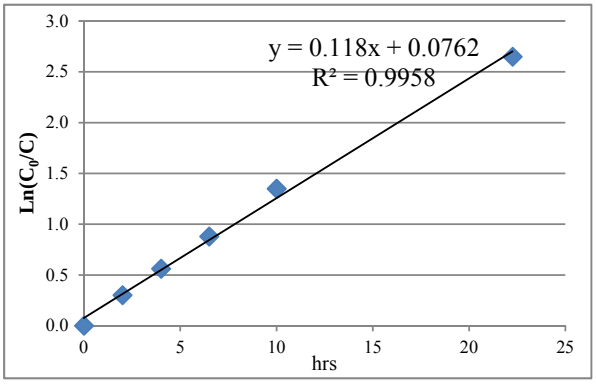


$k_{2,2nd\ order}$=	7.76E-03	$M^{-1}s^{-1}$		k_3=	3.18E-05	s^{-1}



$k_{2,2nd\ order}$=	8.02E-03	$M^{-1}s^{-1}$		k_3=	3.21E-05	s^{-1}

F. Reactions at *pH* 14.0



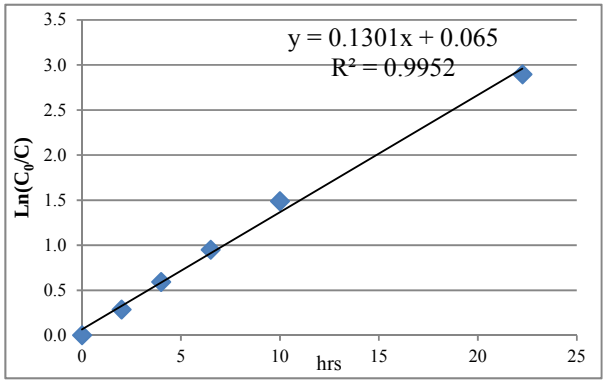
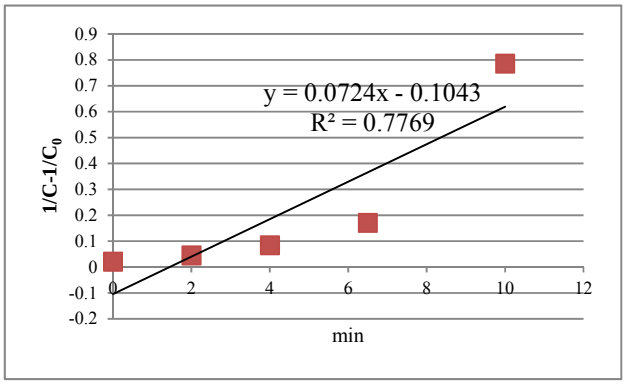


Figure S12. First-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH_2)$ at ***pH*=14.0**, at 21.0 °C.

[SM] = 16.7 mM, conversion = 93%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 27%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 65%
$t_{1/2}$ = 5.9 hrs
Standard Deviation = 0.9513

[SM] = 17.1 mM, conversion = 95%
(dpms)$Pt^{IV}Me(OH)_2$ yield = 29%
(dpms)$Pt^{IV}Me_2(OH)$ yield = 66%
$t_{1/2}$ = 5.3 hrs
Standard Deviation = 1.0488



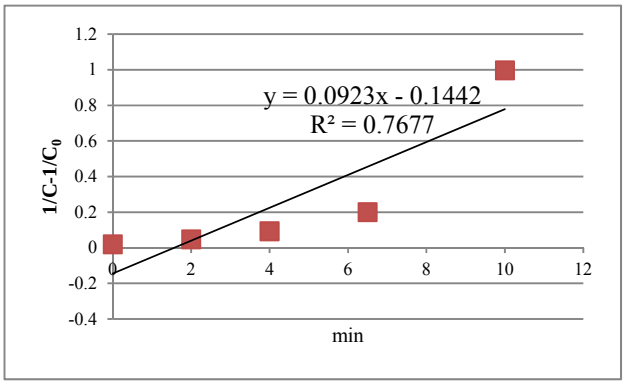
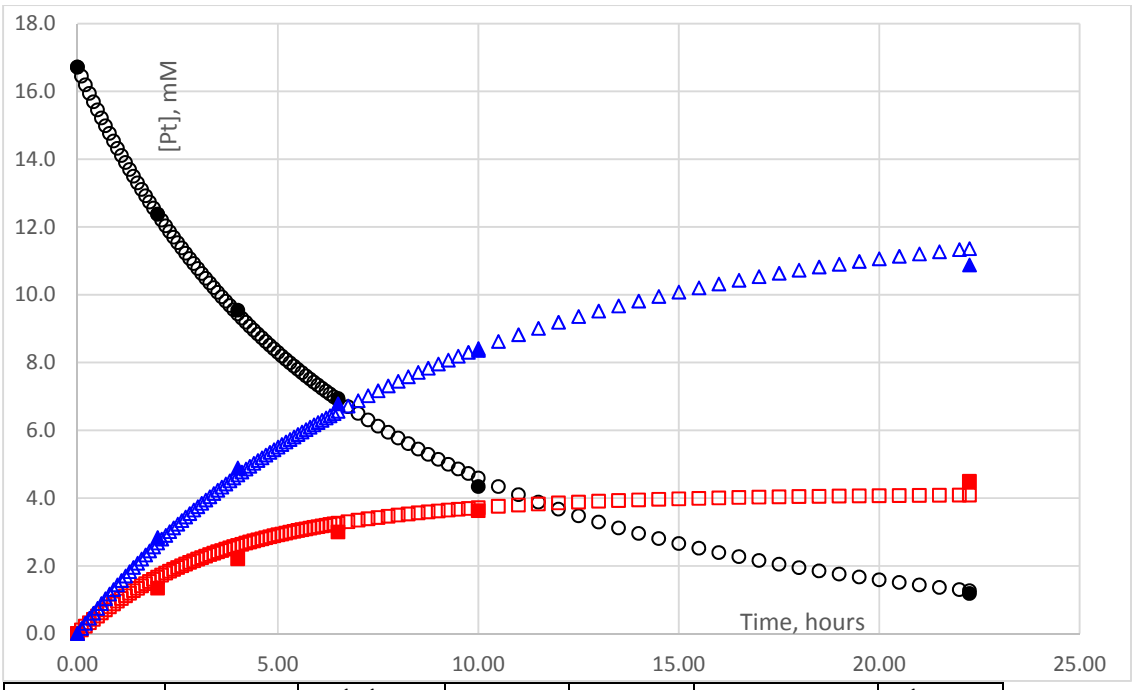


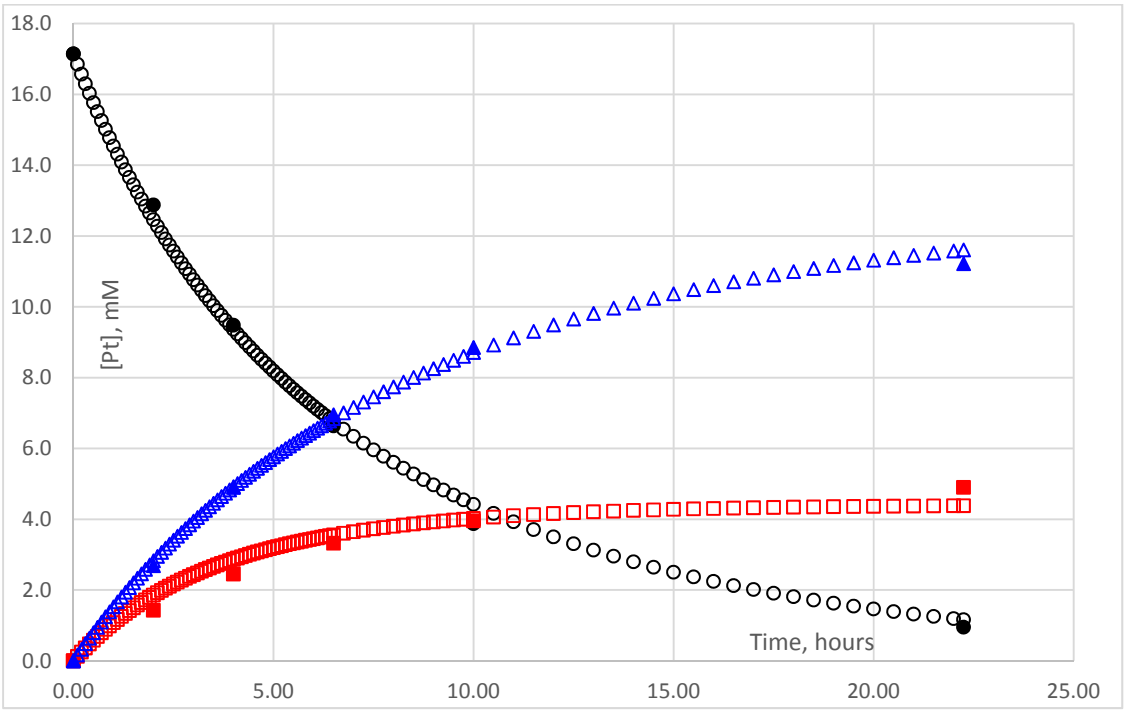
Figure S13. Attempted second-order kinetics plots for disappearance of (dpms)$Pt^{II}Me(OH)$ at ***pH*=14.0**, at 21.0 °C.

Best least square fitting of the experimental data for *pH* = 14.0 achieved by numerical integration of the rate law $-d[2]/dt = k_{2,2nd\ order}[2]^2 + k_3[2]$

circles – [**2**], squares – [**5**], triangles – [**6**]. Empty figures represent calculated concentrations and filled ones – measured in experiment.



$k_{2,2nd\ order}$=	1.09E-03	$M^{-1}s^{-1}$		k_3=	2.56E-05	s^{-1}



$k_{2,2nd\ order}$=	1.17E-03	$M^{-1}s^{-1}$		k_3=	2.66E-05	s^{-1}

Oxidation in the presence of TEMPO

Product distribution in oxidation of (dpms)$Pt^{II}Me(OH)^-$ with O_2 in the presence of TEMPO at pH 6.1, 10.0 and 14.0. For comparison product distribution without TEMPO is also included.

pH	TEMPO (equiv.)	Reaction Time	$LPt^{II}Me(OH_n)^{(2-n)-}$, n = 1, 2 (%)	$LPt^{IV}Me(OH)_2$ (%)	$LPt^{IV}Me_2(OH)$ (%)
6.0	0	1 h 40 min	14 ± 3	85 ± 3	1
6.0	3.4	2 h 37 min	8	88	3
6.0	17.3	2 h 0 min	10	87	0
10.0	0	1 h 30 min	12-13	86-87	2 ± 1
10.0	3.5	1 h 30 min	16	79	5
10.0	17.3	1 h 30 min	16	79	3
14.0	0	22 h 15 min	6 ± 1	28 ± 1	65-66
14.0	3.5	22 h 15 min	9	37	54
14.0	17.3	22 h 15 min	15	33	48

No Me-TEMPO was observed by ^{1}H NMR specroscopy. Spectroscopic data for Me-TEMPO in CDCN are available in.[3]

Conditions	Line width of $Pt^{II}Me$ resonance (Hz)
pH 6.0	1.4
pH 6.0, 17.3 equiv of TEMPO	2.7
pH 10.0	2.2
pH 10.0, 17.3 equiv of TEMPO	2.5
pH 14.0	1.7
pH 14.0, 17.3 equiv of TEMPO	3.2

Separation of the observed first order rate constant $k_{(1+2)}$ into k_1 and $k_{2,1st\ order}$

Separation of $k_{(1+2)}$ into individual rate constants for reactions (1) and (2), k_1 and $k_{2,1st\ order}$, was done assuming an equilibrium distribution of **1** and **2** in reaction mixtures that can be calculated from pK_a for **1**, total concentration [**1**]+[**2**] and a solution *pH*.

Also was assumed that $k_{(1+2)}$ = (fraction of **1**)k_1 + (fraction of **2**)$k_{2,1st\ order}$

The fraction of **2** was calculated for [**1**]+[**2**] = 4.0 mM and is given in Table below. Since $k_{(1+2)}$ does not increase substantially (~38%) when going from *pH* 4.1 to 5.9, in spite of about 100-fold increase in the fraction of **2**, we assume that the second term in the equation above does not contribute noticeably into $k_{(1+2)}$ at pH 4.1. Hence, $k_1 = (2.4\pm0.1)\times10^{-4}$ s^{-1}. The greatest contribution of the second term of the equation above into $k_{(1+2)}$ is expected for *pH* 8.0 with the fraction of **2** as high as 41%. Hence, the most accurate estimate of $k_{2,1st\ order}$ can be obtained from data for *pH* 8.0:

$$(2.6\pm0.1)\times10^{-3} = 59\%\times k_1 + 41\%\times k_{2,1st\ order}.$$

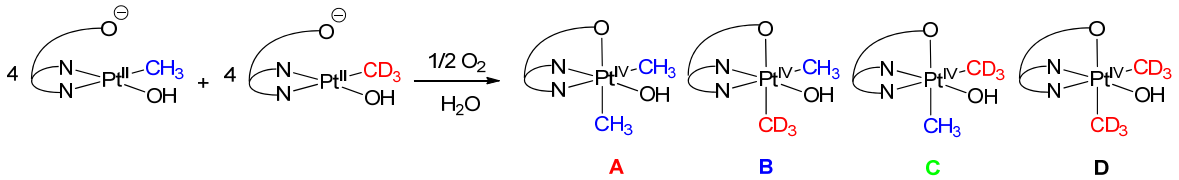
Using $k_1 = (2.4\pm0.1)\times10^{-4}$ s^{-1} we can get $k_{2,1st\ order} = (6.0\pm0.2)\times10^{-3}$ s^{-1}.

To check the validity of the result obtained a $k_{(1+2)}$ was calculated for pH 5.9:

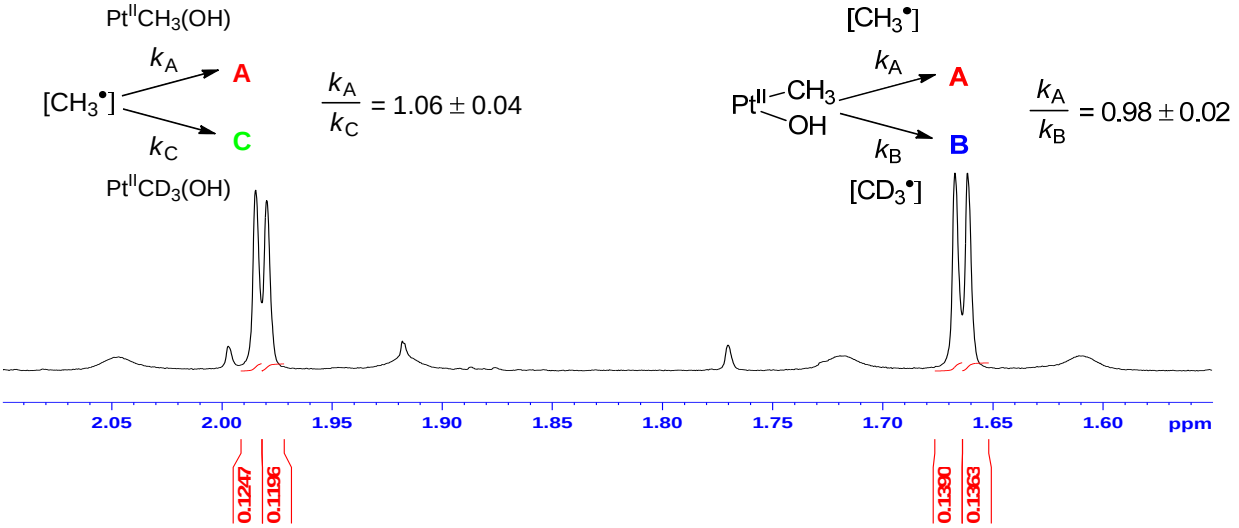
$k_{(1+2),\ calculated} = 99.3\%\%\times(2.4\pm0.1)\times10^{-4} + 0.7\%\times(6.0\pm0.2)\times10^{-3} = (2.8\pm0.1)\times10^{-4}$ s^{-1} which is in a reasonable agreement with the experimental value $(3.3\pm0.2)\times10^{-4}$ s^{-1}.

pH	Observed reaction (1) plus (2) rate constant at $pH \leq 8$, $k_{(1+2)}$, s^{-1}	Fraction of **2**, %	Calculated $k_{(1+2)}$, s^{-1}
4.1	$(2.4\pm0.1)\times10^{-4}$	<0.01%	-
5.9	$(3.3\pm0.2)\times10^{-4}$	0.7%	$(2.8\pm0.1)\times10^{-4}$
8.0	$(2.6\pm0.1)\times10^{-3}$	41%	-

The secondary deuterium kinetic isotope effect for the Pt-to-Pt methyl group transfer

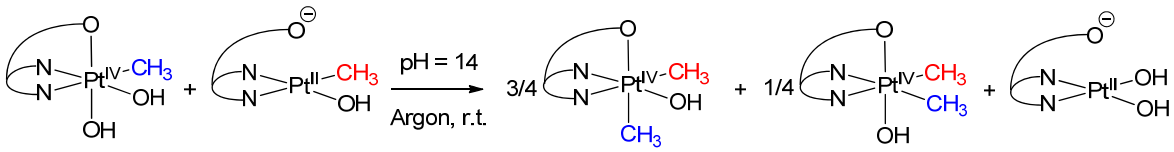


In the argon-filled glove box two Schlenk flasks, equipped with a magnetic stir bars, were charged with 10.2 mg (20 μmol) of K(dpms)$Pt^{II}(Me)_2$ each. Deoxygenated H_2O (0.62 mL) was added to the first Schenk flask and D_2O (0.64 mL) was added to the second Schenk flask. Schlenk flasks were taken out of the box and were kept in the water bath at 40 °C for 6 hrs to give K(dpms)$Pt^{II}CH_3(OH)$ and K(dpms)$Pt^{II}CD_3(OH)$ respectively in quantitative yield. Flasks were brought back inside the glove box, their contents were mixed together and combined with 0.20 mL of 1.00 M NaOH. The mixture was taken out of the glove box, and purged with O_2. Schlenk flask was sealed and the mixture was stirred overnight at 21 °C. Secondary kinetic isotope effect was calculated based on integration of the Pt^{IV}-CH_3 peaks in the upfield region of ^{1}H NMR spectra. Spectra were recorded on 600 MHz NMR spectrometer. ESI-MS spectrum was inconclusive due to overlapping signals of isotopologous Pt^{IV}-Me groups.



Model Studies of Pt-to-Pt Methyl group Transfer

Model study of Methyl group transfer from *C*$_1$-*sym*-(dpms)Pt^{IV}Me(OH)$_2$ to *K*(dpms)Pt^{II}Me(OH) at *pH* = 14



In an argon filled glove box, a solution of *C*$_1$-*sym*-(dpms)Pt^{IV}Me(OH)$_2$ (0.40 mL, 11.0 µmol) in H_2O was combined with K(dpms)Pt^{II}Me(OH) (0.45 mL, 12.3 µmol) in D_2O. *pH* of the reaction mixture (total volume 0.85 mL) was adjusted to *pH* = 14 using 47.6 mg (0.85 mmol) KOH under argon atmosphere. Reaction was transferred into NMR tube with air tight Teflon valve and taken out of the glove box. Methyl group transfer was monitored by ^{1}H NMR spectroscopy over 22 days. Mass balance was calculated based on integration of Pt^{IV}-CH_3 groups relative to 1,4-dioxane.

Table S3. Mass balance at *pH* = 14 calculated based on the integration of the CH_3 groups.

Time (days)	*C*$_1$-*sym*-Pt^{IV}**CH$_3$**(OH)$_2$	Pt^{II}**CH$_3$**(OH)	*C*$_1$-*sym*-Pt^{IV}(**CH$_3$**)$_2$(OH)	*C*$_s$-*sym*-Pt^{IV}(**CH$_3$**)$_2$(OH)	Total
0	0.81	0.96	0.04	0.05	1.86
1	0.77	0.91	0.10	0.05	1.83
2	0.71	0.87	0.18	0.08	1.84
5	0.63	0.73	0.38	0.12	1.86
8	0.51	0.62	0.55	0.17	1.85
10	0.45	0.58	0.67	0.19	1.89
14	0.34	0.46	0.78	0.25	1.83
18	0.26	0.4	0.88	0.28	1.82
22	0.19	0.33	0.98	0.36	1.86

Table S4. Summary of product distribution at *pH* = 14

	Conversion (%)	Yield (%)
C_1-*sym*-LPt^{IV}(CH$_3$)(OH)$_2$	77	-
LPt^{II}CH$_3$(OH)	64	-
C_1-*sym*-LPt^{IV}(CH$_3$)$_2$(OH)	-	53
C_s-*sym*-LPt^{IV}(CH$_3$)$_2$(OH)	-	19

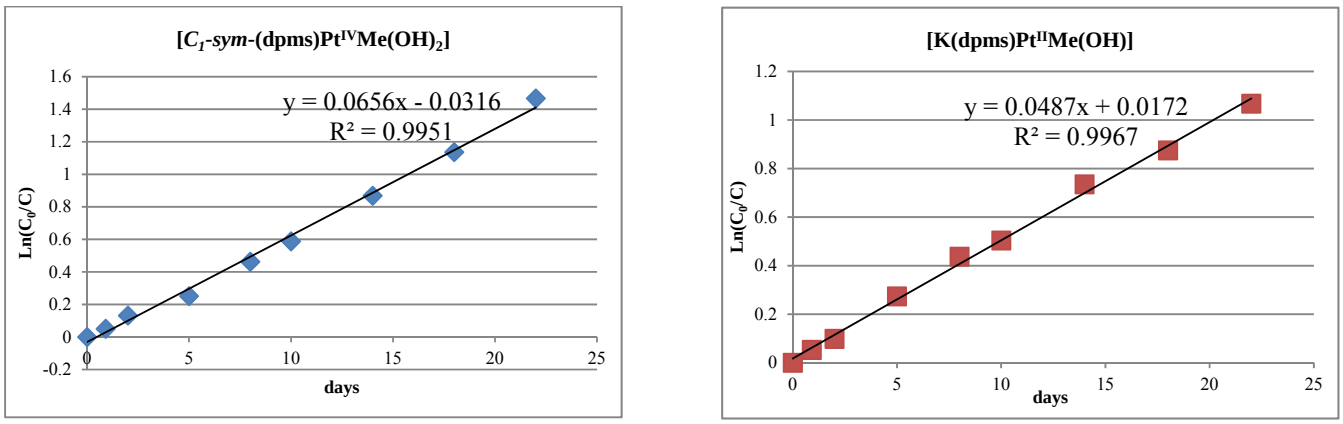


Figure S14. First-order kinetics plot for disappearance of C_1-*sym*-(dpms)Pt^{II}Me(OH)$_2$ (blue) and K(dpms)Pt^{II}Me(OH) (red) at ***pH*=14.0**, ambient temperature.

The reaction rate constant, $k_{2\text{-}5} = 7.59\times10^{-7}$ s^{-1}

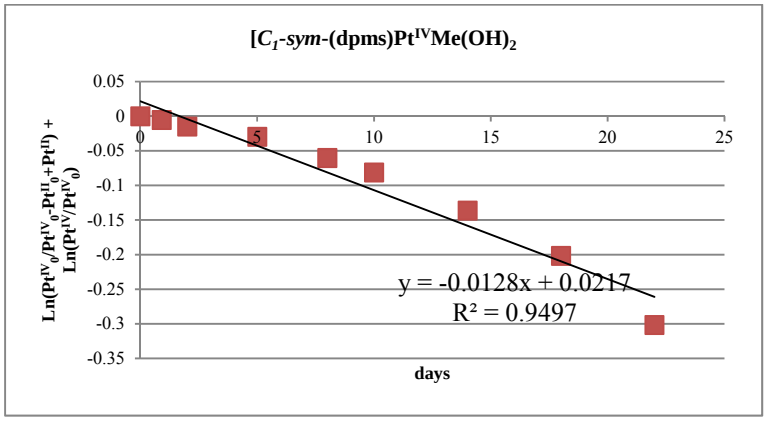
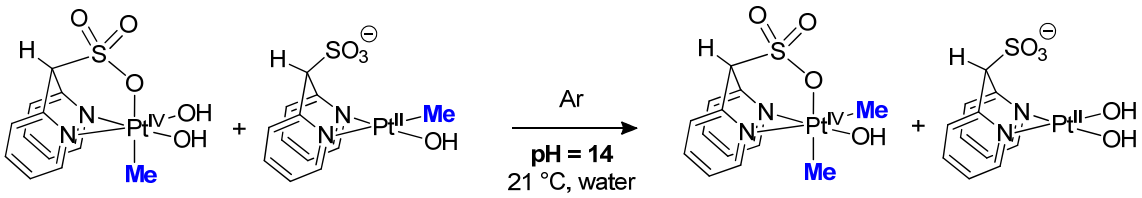


Figure S15. Second-order kinetics plot for disappearance of C_1-*sym*-(dpms)Pt^{II}Me(OH)$_2$ at ***pH*=14.0**, ambient temperature.

Based on the average yield of Me group transfer product (70±1%) and half-life of disappearance of the (dpms)Pt^{II}**CH_3**(OH) under aerobic conditions ($t_{1/2}$ = 5.6 hrs), relative rate of accumulation of *C_1-sym*-(dpms)Pt^{IV}(**CH_3**)$_2$(OH) and *sym*-(dpms)Pt^{IV}(**CH_3**)$_2$(OH) under aerobic conditions is ~30 times faster than in the model study:

pH	Model Reaction t = ~23 °C, C = 23.3 mM	Aerobic Oxidation T = 21 °C, C = 16.7 mM	Relative Rate of Formation of *C_1-sym-*, *C_s-sym*-(dpms)$Pt^{IV}Me_2$(OH)	
			Model Reaction	Aerobic Oxidation
14.0	$k_{2\text{-}5} = 7.59\times10^{-7}$ s^{-1}	$k_3 = (2.61\pm0.05)\times10^{-5}$ s^{-1}	1	34

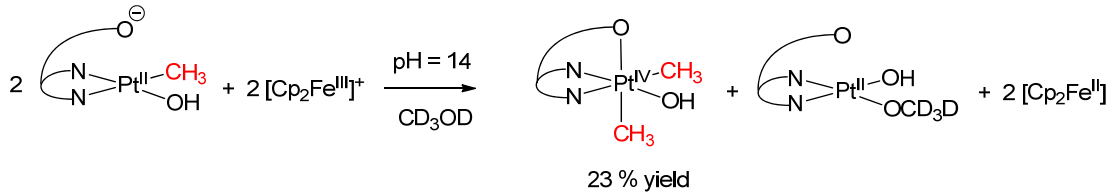
Model study of Methyl group transfer from *C_s-sym*-(dpms)$Pt^{IV}Me(OH)_2$ to *K*(dpms)Pt^{II}Me(OH) at *pH* = 14



In an argon filled glove box, *pH* of *C_s-sym*-(dpms)$Pt^{IV}Me(OH)_2$ (0.45 mL,17.1 µmol) in H_2O was adjusted to *pH* = 14 using 18 mg (0.45 mmol) NaOH under argon atmosphere. In a separate vial, *pH* of K(dpms)Pt^{II}Me(OH) (0.45 mL, 20.9 µmol) was adjusted to *pH* = 14 using 18 mg (0.45 mmol) NaOH. Solutions of *sym*-(dpms)$Pt^{IV}Me(OH)_2$ and K(dpms)Pt^{II}Me(OH) were combined, immediate color change from colorless to yellow was observed. Analysis of the reaction mixture by ^{1}H NMR spectroscopy after a few minutes showed complete consumption of both *C_s-sym*-(dpms)$Pt^{IV}Me(OH)_2$ and K(dpms)Pt^{II}Me(OH). ^{1}H NMR analysis showed presence of K(dpms)Pt^{II}Me(OH) (18% remaining), (dpms)$Pt^{II}(OH)_2^-$ and *C_1-sym*-(dpms)$Pt^{IV}(CH_3)_2$(OH). Yellow color of the solution faded overnight.

In our theoretical paper[4] an experiment with ferrocenium oxidation of **2** is mentioned. Though it is not relevant to the current version of the experimental paper, its description is provided below.

Pt-to-Pt Methyl group Transfer in the Presence of Fc^+



23 % yield

A stock solution of (dpms)$Pt^{II}CH_3(OH)$ in H_2O (9.4 μmol) was evaporated to dryness and redissolved in CD_3OD. $Cp_2Fe^{III}PF_6$ (3.4 mg, 10.3 μmol) was added and solution turned green within minutes and ferrocene precipitate began to form. ^1H NMR spectrum indicated formation of paramagnetic Pt^{III} due to broadening of the signals. After 1 day ^1H NMR showed presence of *C_1-sym*-(dpms)$Pt^{IV}(CH_3)_2(OH)$ in 23 % yield, 16 % of unreacted (dpms)$Pt^{II}CH_3(OH)$ remained in the reaction mixture.

References:

1. a)Vedernikov, A. N.; Fettinger, J. C.; Mohr, F. *J. Am. Chem. Soc.* **2004,** *126*, 11160-11161; b) Vedernikov, A. N.; Binfield, S. A.; Zavalij, P. Y.; Khusnutdinova, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 82-83.

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3. Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2010**, *132*, 7303-7305.

4. Liu, W.-G.; Sberegaeva, A. V.; Nielsen, R. J.; Goddard, W. A. III, Vedernikov, A. N. *J. Am. Chem. Soc.* **2014**, *136*, 2335-2341.